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(54) Title: EMULSION PRESSURE SENSITIVE ADHESIVE

(57) Abstract: High performance pressure sensitive adhesive compositions comprising emulsion polymers and polyurethanes show unexpectedly high levels of adhesion to polar, non-polar and difficult-to-bond substrates. These adhesives possess a combination of excellent peel adhesion and shear properties and exhibit high resistance to water and humidity.

EMULSION PRESSURE SENSITIVE ADHESIVE

FIELD OF THE INVENTION

The present invention relates to a high performance pressure sensitive adhesive composition. More specifically, the invention relates to adhesive compositions comprising an emulsion polymer and a polyurethane dispersion.

BACKGROUND OF THE INVENTION

Pressure sensitive adhesives (PSAs) are a class of adhesive compositions which are applied with pressure, usually finger pressure, and generally do not undergo a liquid-to-solid transition in order to hold materials together. PSAs can be solvent-free natural or synthetic resins having a viscoelastic property termed tack. Tack is a property characterized by the rapid wetting of a substrate by a polymer to form an adhesive bond upon brief contact with the substrate under light pressure. Typical applications for PSAs include pressure sensitive tapes, labels, decals, decorative vinyls, laminates, wall coverings and floor tiles.

Polyacrylates have gained wide acceptance in pressure sensitive adhesive formulations due to their clarity and resistance to oxidation and sunlight. Acrylic copolymer PSAs are available as solution or aqueous polymer emulsions and may also be solid hot melt pressure sensitive adhesives.

Anionic and nonionic emulsifiers are generally employed in acrylic emulsion polymerization reactions to protect the soft pressure sensitive polymers from impact coalescence during the reaction and to stabilize the latex

to provide for good mechanical and storage stability. However, emulsifiers have adverse effects on pressure sensitive polymer emulsion adhesives properties by affecting water resistance, tack and adhesion.

While it is known that tackifiers may be added to acrylic-based PSAs to improve peel adhesion, the addition of tackifiers leads to a reduction in the shear properties and convertability characteristics of the adhesive.

There is thus a need in the art for PSAs which exhibit excellent high performance properties, show superior water and humidity resistance and possess well balanced peel and shear adhesion to a wide variety of substrates, from polar, relatively high energy substrates such as glass and stainless steel, to non-polar, relatively low energy surfaces such as polyolefins.

SUMMARY OF THE INVENTION

The present invention fulfills this need by providing a high performance pressure sensitive adhesive composition that shows a high level of adhesion to difficult-to-bond substrates, possesses excellent peel adhesion and shear properties, and has excellent water and humidity resistance.

One aspect of the invention is directed to a pressure sensitive adhesive comprising, on a dry weight basis, about 30 to about 95% of an emulsion polymer and about 1 to about 50% of an aqueous anionic and/or nonionic dispersion of a polyurethane.

Preferably, the emulsion polymer used to prepare the adhesive is formed from monomers comprising, on a dry weight basis, from about 14 to about 99% of alkyl acrylate monomers. In addition to the alkyl acrylate monomers, the monomer mix used to form the emulsion polymer may further comprise, on a dry weight basis, up to about 30% of vinyl ester monomers, up

to about 30% of alkyl methacrylate monomers, up to about 20% of substituted (meth)acrylamide monomers, up to about 6% of unsaturated carboxylic acid monomers; and/or up to about 6% of hydroxyalkyl(meth)acrylate monomers.

In a preferred embodiment, the emulsion polymer further comprises a surfactant which comprises, based on the total weight of the dry polymer, from about 0.5% by weight to about 1.5% by weight of a sodium dialkylsulfosuccinate; and from about 0.5% by weight to about 1.5% by weight of a tetrasodium (N-dicarboxyalkyl) N-alkyl sulfosuccinamate and up to about 4% by weight of ammonium or sodium salts of sulfated alkylphenoxy poly(ethyleneoxy) ethanol.

In another aspect of the invention, the pressure sensitive adhesive, in addition to the emulsion polymer and the polyurethane dispersion, further comprises, on a dry weight basis, up to about 45% of an aqueous dispersion of a tackifier and/or up to 2% of a crosslinker.

Still another aspect of the invention is directed to a surfactant useful in emulsion polymerization comprising, based on the total weight of the dry polymer, from about 0.5% by weight to about 1.5% by weight of a sodium dialkylsulfosuccinate; from about 0.5% by weight to about 1.5% by weight of a tetrasodium (N-dicarboxyalkyl) N-alkyl sulfosuccinamate, and up to about 4% by weight of ammonium or sodium salts of sulfated alkylphenoxy poly(ethyleneoxy) ethanol.

Yet another aspect of the invention is directed to a method of increasing the shear resistance and humidity resistance of an acrylic emulsion pressure sensitive adhesive. The method comprises forming an acrylic emulsion polymer, which will be used to prepare the adhesive, in the presence of a surfactant composition comprising, based on the total weight of the dry polymer, from about 0.5% by weight to about 1.5% by weight of a sodium dialkylsulfosuccinate, from

about 0.5% by weight to about 1.5% by weight of a tetrasodium (N-dicarboxyalkyl) N-alkyl sulfosuccinamate, and up to about 4% by weight of ammonium or sodium salts of sulfated alkylphenoxy poly(ethyleneoxy)ethanol. A shear resistant and humidity resistant adhesive is prepared by adding a tackifier and/or a crosslinker to the so-prepared polymer emulsion. In a preferred embodiment of this aspect of the invention, the adhesive is prepared by adding a polyurethane dispersion, and optionally tackifier and or crosslinker, to the so-prepared polymer emulsion.

DETAILED DESCRIPTION OF THE INVENTION

The disclosures of all references cited herein are incorporated in their entireties by reference.

Percent by weight means, unless expressly stated otherwise, percent dry weight.

This invention provides pressure sensitive adhesive (PSA) compositions comprising emulsion polymers and polyurethane dispersions and, optionally, tackifiers and/or crosslinkers, which show an unexpectedly high level of adhesion to polar, non-polar and difficult-to-bond substrates. The PSAs of the invention have excellent adhesion to a wide variety of surfaces including polar, relatively high energy, surfaces such as stainless steel and metalized films; and nonpolar, relatively low energy, surfaces such as polyolefin, including polyethylene, polypropylene and polyvinyl chloride. These PSAs have excellent flow, coating and leveling characteristics especially on low energy surfaces and on high speed equipment and show a good balance of shear and peel properties. In addition, superior properties of water and humidity resistance are present.

The present invention also encompasses an improved anionic

surfactant for use in emulsion polymerization. Emulsion polymers prepared with the anionic surfactant described herein, when formulated as pressure sensitive adhesives, provide a product showing stability under high shear conditions, possessing Newtonian-like flow characteristics and having low foam production. In addition, the pressure sensitive adhesives have excellent wet out and leveling characteristic especially on low energy surfaces. Also, the excellent compatibility of ingredients provides a homogeneous system and high clarity coatings.

The pressure sensitive adhesive composition of the invention comprises wherein all percentages are on a dry weight basis,

(a) from about 30 to about 95% by weight of an emulsion polymer formed from a monomer mix comprising (based on the dry weight of the polymer):

(i) about 14 to about 99% by weight alkyl acrylate monomers;

(ii) about 0 to about 30% by weight vinyl ester monomers;

(iii) about 0 to about 30% by weight alkyl methacrylate monomers;

(iv) about 0 to about 20% by weight substituted (meth)acrylamides;

(v) about 0 to about 6% by weight unsaturated carboxylic acids monomers; and

(vi) about 0 to about 6% by weight hydroxyalkyl(meth)acrylate monomers.

(b) about 1 to about 50% by weight of an aqueous anionic and/or nonionic dispersion of polyurethanes;

(c) about 0 to about 40% by weight of an aqueous dispersion of tackifiers; and

(d) about 0 to about 2% by weight of a crosslinker.

The emulsion polymer of the present invention may be prepared by methods familiar to one skilled in the art. By way of example, the emulsion polymer may be prepared with excellent conversion at a reaction temperature ranging from about 70°C to about 85°C, in the presence of from about 0.5 to about 1% by weight, based on the weight of the monomers, of a persulfate or equivalent catalyst, with the monomer mix being fed over a period of about 4 to 5 hours. Reaction pH is from about 2.5 to about 4.0. The reaction may be conducted at ambient pressure and under an inert atmosphere such as nitrogen. Also low temperature polymerization can be used with appropriate initiators such as redox initiators. The reaction mixture is maintained under agitation employing standard mixing techniques.

Suitable polymerization initiators such as water soluble persulfates may be used. Chain transfer agents such as alkyl mercaptans can be employed. Buffers can be used to control pH. Solids content will vary depending upon the selected polymerization conditions. Polymerization conditions are desirably chosen to maintain low levels of coagulum or grit. Polymerization typically occurs under acid conditions and the emulsion formed is neutralized typically with ammonia to a final pH of from about 6 to about 9. Polymers of the invention can be produced at a high solids level, with use of an initial batch of monomers, followed by addition of the balance of the monomers being added to the emulsion reaction system over a period of time.

The monomers employed in the emulsion polymerization process can be added to the reaction mixture in a single stage, or alternatively, can be added to the reaction mixture in a multi-stage addition. The emulsion polymers may be prepared using conventional surfactants.

An emulsion polymer prepared in accordance with the invention preferably has a glass transition temperature of less than about -10°C., even more preferably about -30°C, as measured by differential scanning calorimetry.

Alkyl acrylate monomers suitable for use in this invention include, but are not limited to, alkyl acrylates, and mixture of alkyl acrylates wherein the alkyl group comprises 1 to 8 carbon atoms. Typical, examples of such monomers include n-butyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, and methyl acrylate. A preferred monomer is a mixture of methyl acrylate and butyl acrylate.

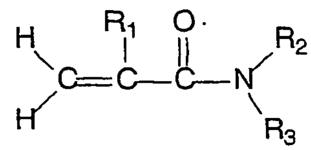
Suitable vinyl monomers include, but are not limited to, vinyl esters containing from 1 to about 16 carbon atoms in the alkyl group of the ester. Typical vinyl esters include vinyl acetate, vinyl butyrate, vinyl propionate, vinyl isobutyrate, vinyl valerate, and vinyl versatate. A preferred vinyl ester for use in the invention is vinyl acetate.

Alkyl methacrylate monomers include, but are not limited to, those wherein the alkyl groups comprise 1 to 10 carbon atoms. Examples include, but are not limited to, methyl methacrylate, propyl methacrylate, hexyl methacrylate, iso-butyl methacrylate. A preferred alkyl methacrylate is methyl methacrylate. Alkyl methacrylate monomers are preferably present in amounts of 10 to 15% by weight based on the total weight of the emulsion polymer.

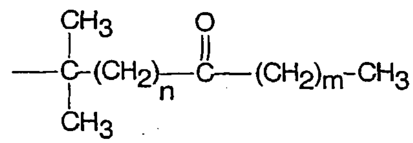
Preferably the total weight percent of the vinyl ester and/or alkyl methacrylate monomers will not exceed 30% by weight of the emulsion polymer.

Examples of suitable substituted (meth)acrylamides for use in the invention include, but are not limited to, acrylamide, methacrylamide, N-tertiary alkyl acrylamide, N-isopropyl acrylamide, dimethyl acrylamide and diacetone

acrylamide and include those having the formula:



where R_1 is H or CH_3, R_2 is H or CH_3, and R_3 is CH_3 or $C(CH_3)_2$-$(CH_2)_n$-CH_3, where n is 0 through 17, or a substituent of the formula:



where n is 1 through 17 and m is 0 through 10.

A preferred substituted acrylamide is N-tertiary octyl acrylamide. Substituted (meth)acrylamide are preferably present in amounts of 10 to 15% by weight based on the total weight of the emulsion polymer.

Examples of suitable unsaturated carboxylic acid monomers include, but are not limited to, acrylic acid, methacrylic acid, and itaconic acid. Acrylic and methacrylic acid are the preferred unsaturated carboxylic acids. Methacrylic acid is most preferred. The unsaturated carboxylic acid monomers are preferably present at about 1 to about 2% by weight, based on the total weight of the emulsion polymer.

Examples of suitable hydroxyalkyl(meth)acrylate monomers include, but are not limited to, hydroxyethylacrylate, hydroxypropyl acrylate, hydroxyethyl methylacrylate and hydroxypropylmethacylate. The hydroxy alkyl(meth)acrylate monomers are preferably present at about 3 to about 4% by weight, based on the total weight of the emulsion polymers.

In addition to the emulsion polymer, the pressure sensitive adhesive compositions of the present invention also comprises an aqueous dispersion of

polyurethanes. The polyurethane component modifies the shear and peel adhesion balance in the adhesive and provides better specific adhesion to polar substrates and nonpolar compositions. Accordingly, the amount of polyurethane added will be an amount effective to balance the shear and peel adhesion properties of the composition. Preferably, the polyurethanes are present at about 5 to about 15% by weight.

Both aliphatic and aromatic poyurethanes, as well a mixtures thereof may be used in the practice of the invention. These polyurethanes may be anionic or nonionic. Such polyurethanes typically will have a number average molecular weight of between about 1000 and 50,000. Examples of polyurethanes usable in the present invention include, but are not limited to, BAYHYDROL DLN and PR240 from Bayer: LUPHEN DDS 3459, 3478, D200A *from* BASF; QW-16-1 *from* SEA, QW-28, QW-18-1 *from* SEA; WITCOBOND W-290H from Witco and the polyurethanes prepared according to U.S. Patent No. 5,717,024. Preferred polyurethanes are polyether and polyester polyurethanes. Due to their low cost and hydrolytic stability, polyether polyurethanes are particularly preferred.

Suitable tackifiers of the present invention will preferably have a softening point of from about 60 to about 100°C. Suitable tackifiers include, but are not limited to, rosin esters, hybrids of rosin based resins and hydrocarbon resins, fully or partially esterified rosins, or hybrids as mentioned above, or conventional blends of a hydrocarbon resin and a rosin based resin. A two component tackifier containing a hydrocarbon resin and a rosin-based resin component can be prepared by mixing a rosin-based resin dispersion with a *hydrocarbon resin dispersion in a suitable ratio. Also useful are wood rosins,* gum rosins, tall oil rosins, fully or partially polymerized rosins, disproportionated

rosins, fully or partially hydrogenated rosins, and other modified and/or stabilized rosins. Useful commercially available tackifiers include, but are not limited to, SNOWTACK 301A, 342A, 385G, and 348A, sold by Akzo Nobel.

Useful hydrocarbon resins include TACOLYN 1070, an aromatic-modified, aliphatic hydrocarbon resin sold by Hercules Incorporated, or ESCOREZ 9271 from EXXON Chemical Co. The useful commercially available hybrids include, but are not limited to, SNOWTACK 810A from Akzo Nobel; TACOLYN 1065 from Hercules; and PERMATAC H712 and H777 from Hercules. Rosin esters are preferred tackifiers for use in the invention and include, among others, the SNOWTACK family of dispersed tackifiers sold by Akzo Nobel; AQUATAC and ZONESTER dispersed tackifiers, such as AQUATAK 6085, sold by Arizona Chemical Company; the TACOLYN and FORAL dispersed tackifiers sold by Hercules; the BERVIK dispersed tackifiers sold by a joint venture company formed by Arizona Chemical and Bervik Kemi of Sweden. Mixtures of tackifiers can also be used. Preferably, the tackifier is present in an amount of between about 10% by weight to about 25% by weight.

The pressure sensitive adhesive composition of the present invention may also comprise a crosslinker. Such crosslinkers may be provided as alkaline aqueous solutions, for example zinc oxide-ammonium complex solutions. Preferred are metal-based crosslinkers such as BACOTE 20, a zirconium-based crosslinker available from Magnesium Elektron, Inc. Preferably, the crosslinker is present in an amount of between about 0.5% by weight to about 1% by weight.

Although standard anionic surfactants may be employed in this invention it has been discovered that a particularly preferred surfactant for use in emulsion polymerization comprises, based on the total dry weight of the

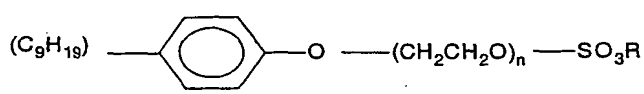
polymer:

(a) about 0 to 4% by weight of ammonium or sodium salts of sulfated alkylphenoxy poly (ethyleneoxy) ethanol wherein the alkyl group may have 1 to 18 carbon atoms;

(b) about 0.5 to 1.5% by weight of a sodium dialkyl sulfosuccinate wherein the alkyl group may have 1 to 18 carbon atoms; and

(c) about 0.5 to 1.5% by weight of a tetrasodium (N-dicarboxy-alkyl) N-alkyl sulfosuccinamate wherein the alkyl group may have 1 to 18 carbon atoms.

Suitable ammonium and sodium salts of sulfated alkylphenoxy poly(ethyleneoxy) ethanol include, but are not limited to, those of the formula:



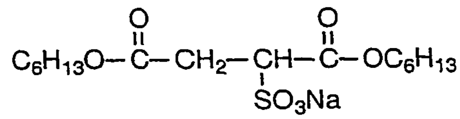
where R is Na or NH_4; and n is an integer of 4 to 30.

Typical examples of ammonium salts of sulfated alkylphenoxy poly(ethyleneoxy) ethanol include AEROSOL NPES-430, AEROSOL NPES-2030, AEROSOL NPES-3030, AEROSOL NPES-930, AEROSOL OT-75-PG, AEROSOL 22, all available from Cytec Industries, Inc. Preferred is AEROSOL NPES 930, an ammonium salt of sulfated nonyl phenoxy poly(ethyleneoxy) ethanol.

In the present invention, it is preferred that the total ammonium and/or sodium salt of sulfated alkylphenoxy poly(ethyleneoxy) ethanol be 1 to 2 weight percent of the total weight of the polymer.

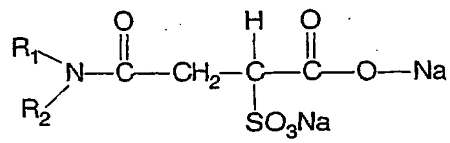
A typical, non limiting, example of a sodium dialkyl sulfosuccinate is AEROSOL MA-80-I, which is available from Cytec Industries, Inc., and has the

formula:

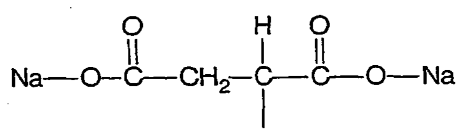


Preferably, the sodium dialkyl sulfosuccinate is present at between 0.5 to 1.0% by weight.

Non-limiting examples of suitable tetrasodium (N-dicarboxy-alkyl) sulfosuccinamates include those with 1 to 18 carbon atoms in the alkyl group, and include those of the formula:



where, R_1 is



and R_2 is octadecyl ($C_{18}H_{37}$).

The pressure sensitive adhesive composition of the present invention may be prepared by formation of the emulsion as discussed above, followed by adjusting its pH to between about 6 and 9 (preferably by addition of ammonia, with agitation), and the tackifier added by any method known to one skilled in the art using adequate mixing. The aqueous polyurethane dispersion may be added before, after or simultaneously with the tackifier, once again with adequate mixing. The optional crosslinker solution, if used, is then slowly added with agitation.

Other additives well known in the art, for example wetting agents, thickeners, antifoaming agents (such as that sold under the trademark DEEFO 215 by Ultra Additives), preservatives, etc., may be added as appropriate for specific applications.

A coater ready pressure sensitive adhesive composition in accordance with the present invention will have high PSA performance, especially on low surface energy surfaces, with excellent flow, coating and leveling characteristics, when applied on high speed equipment.

The pressure sensitive adhesive compositions of the present invention are useful in a wide range of applications. Such applications include, but are not limited to, tapes, stickers, labels, decals, decorative vinyls, laminates, wall coverings and floor tiles.

The present invention provides pressure sensitive adhesives which exhibit excellent high performance properties with well balanced peel and shear adhesion to a wide variety of substrates, from polar, relatively high energy substrates such as glass and stainless steel, to non-polar, relatively low energy surfaces such as polyolefins. The pressure sensitive adhesives of the present invention also have been observed to possess superior properties of water and humidity resistance. While has been observed that modification to the surfactant composition results in improvement of adhesive properties, such as shear, and humidity resistance, the addition of a poylurethane dispersion results in further improvement.

The adhesives of the present invention exhibit good aging characteristics and show no edge ooze or bleed as part of a release liner-adhesive-facestock laminate. In adhesive construction, including label facestock and release liner, the adhesives provide excellent high speed label

converting characteristics, such as die cutting.

The invention will be described further in the following examples, which are included for purposes of illustration and are not intended, in any way, to be limiting of the scope of the invention.

EXAMPLES

Pressure sensitive adhesive compositions were prepared using emulsion polymers prepared as described in Examples 1, 2 and 3. Tackifier was then added to the emulsion polymer (Examples 6-10 and 12-32) with adequate mixing. An aqueous polyurethane dispersion (Examples 7-32) and/or crosslinker (Examples 7-10, 13-16, 24-32) was then added under adequate mixing.

The emulsion polymers and the pressure sensitive adhesives produced from them were evaluated using the following adhesive test procedures.

TESTING PROCEDURES

Peel

180° Peel was tested using the method described by the Pressure sensitive Tape Council in PSTC-1. The test involves peeling the tape off a substrate at 180° angle after application under relatively light pressure. Testing was done to allow 20 minutes (initial peel), 24 hour and one week contact of the adhesive with the test panel. The results are reported as the force required to remove the tape, measured in grams per inch width.

Shear Adhesion

Shear adhesion was measured according PSTC No. 7 using a 1,000 gram (g) mass at room temperature. The bonded area was 1 inch x 0.5 inch. The results are reported as the time required for the bond to fail.

Glass Transition

Glass transition temperature was measured by differential scanning calorimetry.

Aging Conditions

Aging studies were conducted under the conditions reported in the Table.

In the following examples, all parts are by dry weight and all temperatures in degrees Celsius, unless otherwise indicated.

EXAMPLE 1

Preparation of Emulsion Polymer A

This example illustrates the process of preparing a representative emulsion polymer, designated herein and in Tables 1, 2 and 5 as polymer A. This polymer was prepared without a substituted amide in the monomer composition. The reaction was carried out in a 3-liter, 4-neck reactor equipped with a reflux condenser, a thermocouple, a pitched turbine agitator and nitrogen inlet tube. The following charges were prepared:

(A) 210 g water, 1.8 g ammonium persulfate, 1.2 g AEROSOL MA-80-I (80% surfactant), 2.4 g WITCOLATE D51-53 (34% surfactant), 1.2 g sodium bicarbonate.

(B) 54 g butyl acrylate, 6 g methyl acrylate.

(C) Monomer pre-emulsion was made of two parts: surfactant mixture of 210 g water, 9 g AEROSOL NPES 930 (30% surfactant), 3 g AEROSOL MA-80-I, 3 g EMCOL K8300, and monomer mixture of 486 g butyl acrylate, 54 g methyl acrylate, 12 g methacrylic acid,

12 g hydroxyethyl acrylate.

(D) 48 g water, 2.4 g ammonium persulfate, 1.2 g AEROSOL 22 (35% surfactant).

(E) 24 g water, 1.2 g 5-butyl hydrogen peroxide, 1.2 AEROSOL OT-75-PG (75% surfactant).

(F) 36 g water, 1.2 g sodium formaldehyde sulfoxylate, 1.2 g AEROSOL 22.

Charge A was added into reactor with low agitation, about 100rpm. The contents were heated to 60°C, and charge B was slowly added, and agitation was increased to 250 rpm. Charge C was prepared from two parts by slowly adding monomer mixture to water phase surfactant mixture under agitation to form pre-emulsion. The contents temperature was raised to 70°C. After initiation the reaction temperature was allowed to increase to 85°C, and maintained at 80 to 85°C. The contents were held at this temperature for the next 20 minutes, and the delayed charges C and D were started and added uniformly over a 4.5 hour period. After the addition was completed at 80°C, the reaction temperature was reduced to 65°C, charges E and F were added. Thirty minutes later, the mixture was cooled and discharged.

EXAMPLE 2

Preparation of Emulsion Polymer B

This example illustrates the process of preparing a representative emulsion polymer, designated herein and in Tables 1-4 as polymer B. This polymer was prepared with a substituted amide in the monomer composition. The reaction was carried out in a 3-liter, 4-neck reactor equipped with a reflux condenser, a thermocouple, a pitched turbine agitator and nitrogen inlet tube. The following charges were prepared:

(A) 210 g water, 1.8 g ammonium persulfate, 1.2 g AEROSOL MA-80-I (80% surfactant), 2.4 g WITCOLATE D51-53 (34% surfactant), 1.2 g sodium bicarbonate.

(B) 54 g butyl acrylate, 6 g methyl acrylate.

(C) Monomer pre-emulsion was made of two parts: surfactant mixture of 210 g water, 9 g AEROSOL NPES 930 (30% surfactant), 3 g AEROSOL MA-80-I, 3.0 EMCOL K8300, and monomer mixture of 6.0 g sodium vinyl sulfonate (25%), 486 g butyl acrylate, 60 g t-octyl acrylamide, 54 g methyl acrylate, 12 g methacrylic acid, 12 g hydroxyethyl acrylate.

(D) 48 g water, 2.4 g ammonium persulfate, 1.2 g AEROSOL 22 (35% surfactant).

(E) 24 g water, 1.2 g *t-butyl hydrogen peroxide*, 1.2 g AEROSOL OT-75-PG (75% surfactant).

(F) 36 g water, 1.2 g sodium formaldehyde sulfoxylate, 1.2 g AEROSOL 22.

Charge A was added into reactor with low agitation, about 100 rpm. The contents were heated to 60°C, and charge B was slowly added, and agitation was increased to 250 rpm.

Charge C was prepared from two parts by slowly adding monomer mixture to the water phase surfactant mixture under agitation to form a pre-emulsion. While blending the monomer mixture t-octyl acrylamide was dissolved in butyl acrylate with adequate agitation. The contents temperature was raised to 70°C. After initiation the reaction temperature was allowed to increase to 85°C and maintained at between 80° and 85°C. The contents were held at this temperature for the next 20 minutes, and the delayed charges C and

D were started and added uniformly over a 4.5 hour period. After the addition was completed at 80°C, the reaction temperature was cooled and discharged.

EXAMPLE 3

Preparation of Emulsion Polymer C

This example illustrates the process of preparing a representative emulsion polymer, designated herein and in Tables 1 and 4 as polymer C. This polymer was prepared with methyl methacrylate in place of methyl acrylate in the monomer composition. The reaction was carried out in a 2-liter, 4-neck reactor equipped with a reflux condenser, a thermocouple, a pitched turbine agitator and nitrogen inlet tube.

The following charges were prepared:

(A) 200 g water, 1.5 g AEROSOL MA (80% surfactant), 1.5 g sodium bicarbonate.

(B) 15 g water, 3.5 g ammonium persulfate.

(C) Monomer pre-emulsion was made in two parts: surfactant mixture of 179 g water, 7.5 g AEROSOL NPES-930 (30% surfactant), 3.5 g AEROSOL MA-80I (80% surfactant), 15 g WITCOLATE D51-53 (34% surfactant), 3.0 g AEROSOL 22 (35% surfactant), and monomer mixture of 450 g butyl acrylate, 50 g methyl methacrylate, 15 g methacrylic acid, 5 g 2-hydroxyethyl acrylate.

(D) 12.5 g water, 1.0 g t-butyl hydrogen peroxide, 1.0 g AEROSOL OT-75 (75% surfactant).

(E) 25 g water, 1.0 g sodium formaldehyde sulfoxylate.

(F) 35.5 g water

(G) 8.5 g water, 2.0 g DEEFO 215 (defoamer)

Charge A was added into reactor with low agitation, about 100 rpm. The contents were heated to 65ºC, agitation was increased to 300 rpm and charge B was added.

Charge C was prepared from two parts by slowly adding the monomer mixture to the water phase surfactant mixture under agitation to form the pre-emulsion. At the start of the 3 hour monomer slow add, the reaction was raised to 80ºC. At the end of the monomer slow add, the reaction was cooled to 65ºC. Charge D is added as a shot. Charge E is added over 40 minutes. Charge F is added as a shot. The reaction is then cooled to 38ºC. Charge G is added as a shot. The reaction is mixed for 10 minutes and finally discharged.

The physical properties of polymers A, B and C are listed in Table 1.

TABLE 1

Polymer	% Solids	Brookfield Viscosity (cps)	Tg °C	pH	Grit %	Particle Size (nm)
A	52.5	200	-39	2.8	0.003	164
B	54.3	400	-31	2.8	0.005	168
C	51.9	67	-32*	3.9	0.0185	248

*predicted value

In the following Examples 4-32, the tackifier was AQUATAC 6085; the polyurethane dispersion was prepared as described in U.S. Patent No. 5,717,024, *unless otherwise noted (i.e., Examples 24-32), and the crosslinker* was BACOTE 20. All percentages are stated on a dry weight basis.

EXAMPLES 4-23

Various levels of tackifiers, polyurethanes and crosslinkers were

added to Polymers A, B and C and their peel and shear strength evaluated.

Examples 4, 5 and 6, which contain no polyurethane dispersion component, are presented for purposes of comparison. The results are summarized in Tables 2, 3 and 4.

Table 2

EXAMPLES	4	5	6	7	8	9	10
Acrylic Polymer	A	B	B	A	A	A	A
Parts Acrylic Polymer	100	100	100	100	100	100	100
Parts Tackifier	--	--	35	5	10	15	35
Parts Polyurethane	--	--	--	6.6	6.6	6.6	6.6
Parts Crosslinker	--	--	---	0.6	0.6	0.6	0.6
Stainless Steel Shear (hours)	2.7	11.8	3.92	50.9	49.7	14.6	12.7
High Density Polyethylene							
Initial peel (g/in)	765	892	1750	805	901	901	763
24 hr @ RT	865	967	2284	884	1044	1097	900
1 wk @ RT	1074	1031	2104	929	1097	1151	941
24 hr. @ 158°F	903	719	1572	812	868	801	854
1 week @ 158°F	944	696	1298	668	810	929	862
24 hr. @ high humidity (100°F, 95% RH)	1222	1100	2171	840	1055	1167	1289
1 week @ high humidity (100°F, 95% RH)	1191	996	1970	922	965	1037	1348

Table 3

EXAMPLES	11	12	13	14	15	16	17
Acrylic Polymer	B	B	B	B	B	B	B
Parts Acrylic Polymer	100	100	100	100	100	100	100
Parts Tackifier	--	5	5	10	15	35	5
Parts Polyurethane	6.6	6.6	6.6	6.6	6.6	6.6	5
Parts Crosslinker	--	--	0.6	0.6	0.6	0.6	--
Stainless Steel Shear (hours)	16.6	59.8	145.3	79.2	40.5	48.8	35.9
High Density Polyethylene Initial peel (g/in) 24 hr @ RT 1 wk @ RT	 731 801 1363	 772 1230 1193	 768 1195 1125	 1042 1083 1146	 994 1266 1115	 773 842 900	 965 1105 1113
24 hr. @ 158°F 1 week @ 158°F	737 773	726 832	670 739	717 753	884 800	850 796	784 865
24 hr. @ high humidity (100°F, 95% RH) 1 week @ high humidity (100°F, 95% RH)	1117 1244	1248 1144	1168 1178	1236 1193	1281 1217	1134 1059	1154 1306

Table 4

EXAMPLES	18	19	20	21	22	23
Acrylic Polymer	B	C	C	C	C	none
Parts Acrylic Polymer	100	100	100	100	100	--
Parts Tackifier	35	15	56.7	37.8	113.5	31
Parts Polyurethane	6.5	8	63.5	126.9	63.5	69
Parts Crosslinker	--	--	--	--	--	--
Stainless Steel Shear (hours)	5.5	20.4	>150	>150	>150	>150
High Density Polyethylene Initial peel (g/in) 24 hr @ RT 1 wk @ RT	 1239 1349 1654	 540 567 571	 355 349 396	 144 134 205	 320 447 468	 10 10 3
24 hr. @ 158°F 1 week @ 158°F	1746 1308	555 566	444 437	151 165	445 579	55 124
24 hr. @ high humidity (100°F, 95% RH) 1 week @ high humidity (100°F, 95% RH)	1970 2181	695 630	527 497	367 444	467 529	27 77

While Examples 4 and 5 show good humidity resistance, they show poor shear. Examples 4 and 5 are typical high performance pressure sensitive adhesives which also show adequate humidity resistance, which is attributed to the particular surfactant composition uses to prepare the acrylic polymer. Example 6, containing tackifier, has improved peel strength over Example 5, but decreased shear performance. This trend is typical of pressure sensitive adhesives where tackifier is added to improve peel but there is a decrease in shear performance.

The results of examples 7 to 22 show the pressure sensitive adhesives of this invention have a superior balance of shear, peel adhesion and humidity resistant properties when compared with the Comparative Examples 4, 5 and 6.

Another benefit obtained from using a polyurethane dispersion in an acrylic system is increased humidity resistance. This can be seen, e.g., by comparing Comparative Example 4 and Example 7. Humidity resistance peel test can be qualitatively measured by examining the mode of failure that the coated adhesive exhibits. Adhesive "failure" is characterized as being a good result, because no adhesive has transferred to the testing (or application) surface. In contrast, adhesive "transfer" is characterized as a bad result because, while the peel value still may be acceptable, the adhesive has fully transferred to the testing (or application) surface. And with continued aging, the peel value will gradually decrease to the point that the substrate will fall off the application or testing surface because the adhesive is no longer bonded to the substrate. Whereas Comparative Example 4, formulated without a polyurethane dispersion, exhibits adhesive transfer when conditioned in humidity conditions (100ºF, 95% relative humidity) for 1 week, Example 7, formulated with a polyurethane dispersion, tackifier and crosslinker, exhibits

adhesive failure under the same aging conditions. While it is known to one skilled in the art that the addition of a crosslinker can increase humidity resistance, a consequence is that the overall peel values drop significantly. But as evident by the data, Example 7 exhibits zero to minimal decrease in peel strength with the needed adhesive "failure" as the mode of failure at humidity aging.

EXAMPLES 24-32

In Examples 24 to 32, Polymer A, prepared according to Example 1, was formulated into an adhesive using the following different polyurethane dispersions, designated P1 to P10.

P1 - BAYHYDROL PR240

P2 - WITCOBOND W-290H

P3 - BAYHYDROL DLN

P4 - QW-28

P5 - QW-16-1

P6 - QW-18-1

P7 - LUPHEN DDS3459

P8 - LUPHEN D200A

P9 - LUPHEN DDS 3418

Examples 24 to 32, set forth in Table 5, demonstrate the effectiveness of different polyurethane dispersions in conjunction with tackifier in the pressure sensitive adhesives of this invention.

Table 5

EXAMPLE	24	25	26	27	28	29	30	31	32
Acrylic Polymer	A	A	A	A	A	A	A	A	A
Polyurethane	P1	P2	P3	P4	P5	P6	P7	P8	P9
Parts Acrylic Polymer	100	100	100	100	100	100	100	100	100
Parts Tackifier	35	35	35	35	35	35	35	35	35
Parts Polyurethane	6.6	6.6	6.6	6.6	6.6	6.6	6.6	6.6	6.6
Parts Crosslinker	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Stainless Steel Shear (hrs)	12.9	6.9	9.8	7.3	10.1	6.3	5.5	8.3	7.7
High Density Polyethylene initial peel 24 hr @ RT 1 wk @ RT	1246 1383 1460	1534 1249 2171	1249 1215 1953	1271 1445 1891	1195 1471 1970	1261 1406 2177	1117 1456 1824	1090 1350 1717	1128 1379 1698
24hr @ 158°F 1wk @ 158°F	1138 1017	1234 1003	1181 923	1118 1060	1335 1254	1310 1105	1393 1090	1282 1110	1323 1170
24 hr @ high humidity (100°F, 95% RH) 1 wk @ high humidity (100°F, 95% RH)	1764 1687	1770 1449	1664 1553	1905 1840	1929 1680	1984 1946	1930 1719	1647 1514	1588 1816

Many modifications and variations of this invention can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. The specific embodiments described herein are offered by way of example only, and the invention is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled.

CLAIMS:

1. A pressure sensitive adhesive composition comprising

about 30 to about 95% by weight, on a dry weight basis, of an emulsion polymer and

about 1 to about 50% by weight, on a dry weight basis, of an aqueous anionic and/or nonionic dispersion of a polyurethane.

2. The adhesive of claim 1 further comprising

up to about 45% by weight, on a dry weight basis, of an aqueous dispersion of a tackifier and/or

up to 2% by weight, on a dry weight basis, of a crosslinker.

3. The adhesive of claim 1 wherein the emulsion polymer comprises from about 14 to about 99 % by weight, on a dry weight basis, of alkyl acrylate monomers.

4. The adhesive of claim 3 wherein the emulsion polymer further comprises

up to about 30% by weight, on a dry weight basis, of vinyl ester monomers,

up to about 30% by weight, on a dry weight basis, of alkyl methacrylate monomers,

up to about 6% by weight, on a dry weight basis, of unsaturated carboxylic acid monomers; and/or

up to about 6% by weight, on a dry weight basis, of hydroxyalkyl(meth)acrylate monomers.

5. The adhesive of claim 4 wherein the combined percentage by weight of the vinyl ester monomers and the alkyl methacrylate monomers is less than about 30%.

6. The adhesive of claim 4 wherein the alkyl acrylate monomers comprise a mixture of methyl acrylate and butyl acrylate monomers.

7. The adhesive of claim 4 wherein the vinyl ester monomers comprise vinyl acetate monomers.

8. The adhesive of claim 4 wherein the emulsion polymer comprises from about 1 to about 2% by weight of the unsaturated carboxylic acid monomer.

9. The adhesive of claim 4 wherein the emulsion polymer comprises about 3 to about 4% by weight of the hydroxyalkyl(meth)acrylate monomer.

10. The adhesive of claim 2 comprising about 10 to about 25% by weight of the aqueous dispersion of tackifiers.

11. The adhesive of claim 1 comprising about 3 to about 30% by weight of the aqueous anionic and/or nonionic dispersions of polyurethanes.

12. The adhesive of claim 1 wherein the polyurethane is a polyether polyurethane.

13. The adhesive of claim 2 comprising about 0.1 to about 1% by weight of the crosslinker.

14. An article of manufacture comprising the adhesive of claim 1.

15. The adhesive of claim 4 wherein the emulsion polymer further comprises a surfactant which comprises, based on the total weight of the dry polymer,

from about 0% by weight to about 4% by weight of ammonium or sodium salts of sulfated alkylphenoxy poly(ethyleneoxy) ethanol;

from about 0.5% by weight to about 1.5% by weight of a sodium dialkylsulfosuccinate; and

from about 0.5% by weight to about 1.5% by weight of a tetrasodium (N-dicarboxyalkyl) N-alkyl sulfosuccinamate.

16. A surfactant useful in emulsion polymerization comprising, based on the total weight of the dry polymer,

from about 0% by weight to about 4% by weight of ammonium or sodium salts of sulfated alkylphenoxy poly(ethyleneoxy) ethanol;

from about 0.5% by weight to about 1.5% by weight of a sodium dialkylsulfosuccinate; and

from about 0.5% by weight to about 1.5% by weight of a tetrasodium (N-

dicarboxyalkyl) N-alkyl sulfosuccinamate.